

**United States Environmental Protection Agency
Region 6
Compliance Assistance and Enforcement Division
1445 Ross Avenue, Suite 1200
Dallas, Texas 75202**

Crossett, AR Hydrogen Sulfide Air Sampling Report

**Crossett, Ashley County, Arkansas
Dates of Monitoring: January 13 - June 30, 2017**

Table of Contents

Introduction.....	3
Background.....	3
Environmental Justice History	3
Facility Details	4
Hydrogen Sulfide	5
EPA’s Passive H ₂ S Air Monitoring	7
Sample Site Selection	7
Site Assessment – September 2016.....	7
Site Assessment – October 2016.....	8
Final Site Selection for Passive Sampling	8
Methodology	11
Results.....	11
Surge Basin Outlet (SBO).....	15
Aeration Stabilization Basin (ASB)	16
East and West Ash Basins.....	17
Community Monitors	19
Air Dispersion Modeling	20
Model Comparisons and Source Apportionment	20
Community Health Considerations	22
Conclusions.....	23
APPENDICES	24
Appendix A - EPA Office of Air Quality Planning and Standards (OAQPS) Modeling Report	
Appendix B - EPA Hydrogen Sulfide Monitoring Quality Assurance Project Plan	
Appendix C - EPA Geospatial Monitoring of Air Pollutants (GMAP) Monitoring Report	
Appendix D - Hydrogen Sulfide Air Sample Results for Community Monitors	
Appendix E - Agency for Toxic Substances and Disease Registry (ATSDR) Hydrogen Sulfide Fact Sheet	

Introduction

The United States Environmental Protection Agency (EPA) conducted air sampling in Crossett, Arkansas, between January and June of 2017. The sampling was conducted to determine emission sources of airborne hydrogen sulfide (H₂S) in the wastewater treatment (WWT) system at the Georgia Pacific (GP) facility in Crossett, AR and to evaluate the potential for exposure in the community. This report summarizes the results of the EPA's hydrogen sulfide air monitoring conducted along GP's WWT system and in surrounding Crossett neighborhoods.

Background

Environmental Justice History

Although community environmental concerns within the town of Crossett have existed for decades, they were highlighted at an EPA Region 6 hosted Environmental Justice Training Workshop in the summer of 2013. At this workshop, a community representative from Crossett spoke about the community's concerns with air emissions and water discharges from the GP facility. In February 2014, EPA Region 6 visited Crossett, toured the community, and participated in a community meeting hosted by the local group Crossett Concerned Citizens for Environmental Justice (CCCEJ). In April of 2014, a second community meeting was held and included participants from the City of Crossett, the Arkansas Department of Environmental Quality (ADEQ), the Arkansas Department of Health (ADH), and EPA Region 6. In February 2015, at the request of EPA Region 6, EPA's National Enforcement Investigation Center (NEIC) conducted concurrent inspections of both the GP Paper Operations and GP Chemical Plant. Preliminary areas of non-compliance and areas of concern were noted, and are being addressed by GP and EPA Region 6 Enforcement.

Residents living near the GP complex have repeatedly complained of frequent breathing problems, eye and throat irritation, corroded HVAC systems and vehicles, and bad smells. Hydrogen sulfide (H₂S), one of the common chemicals generated at pulp and paper mills, could potentially cause some of those problems. In response to community concerns and in cooperation with EPA Region 6, ADEQ, and ADH, GP has been voluntarily conducting an ambient air monitoring assessment for H₂S in Crossett, beginning in October 2014. GP's H₂S air monitor analyzes the air continuously, and takes a reading every minute. It is located about one-half mile north of the WWT clarifier, at the southern end of Penn Road on GP's northern fence line. The results from this monitor are publically available on ADEQ's website (https://www.adeq.state.ar.us/air/compliance/georgia_pacific.aspx). When the monitor detects H₂S levels above the Agency for Toxic Substance and Disease Registry (ATSDR)¹ acute

¹ ATSDR Toxicological Profile for Hydrogen Sulfide and Carbonyl Sulfide
<https://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=389&tid=67>

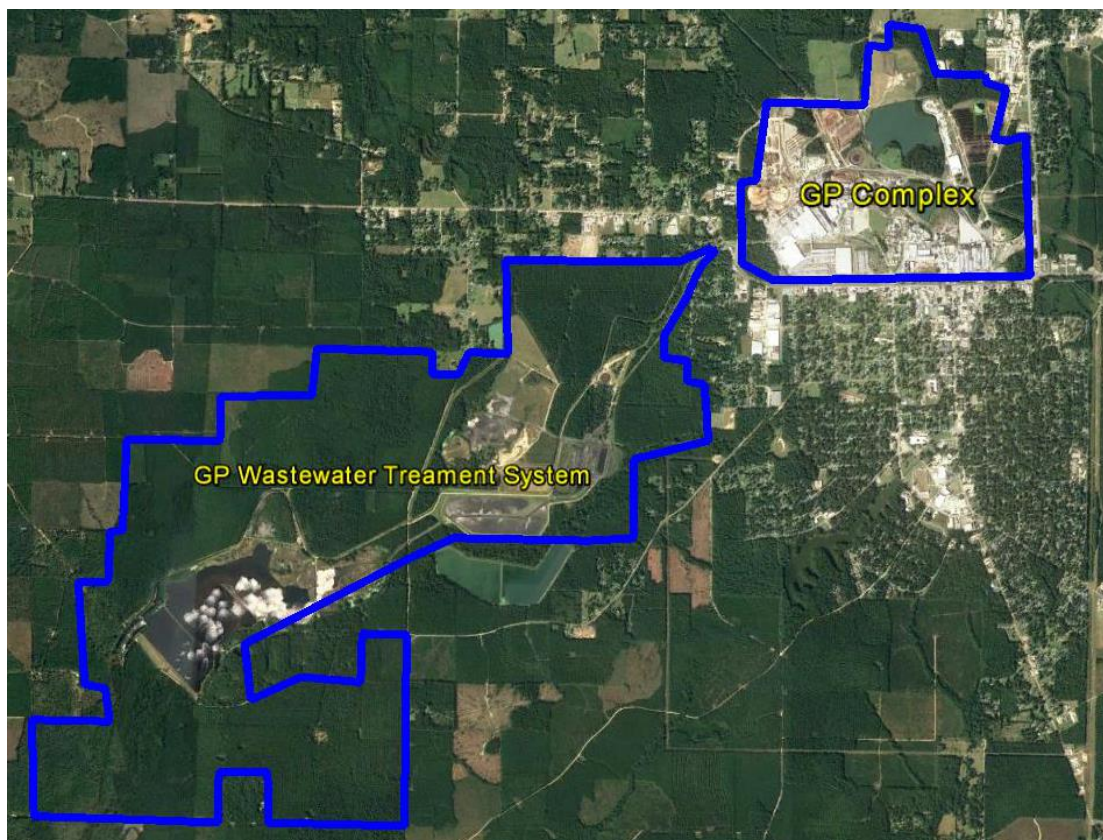
minimal risk level (MRL) of 70 parts per billion (ppb), a special report is generated and posted on the above website. A more detailed explanation about exposure and health risks can be found in Appendix A, (page 7).

Facility Details

GP is a wholly owned subsidiary of Koch Industries, Inc., a private company based in Wichita, Kansas. The large complex in Crossett is roughly 1.5 mile (east/west) by 1 mile (north/south) in size. The GP Complex includes or included a log storage and processing mill, plywood plant, stud plant, pulp and paper plant and a chemical plant. The complex operates year round.

GP's Paper Operations consist of a kraft pulp mill and a bleach plant, located at 100 Mill Supply Road in Crossett, AR. GP's operations began as a saw mill in 1894, and became the Crossett Lumber Company in 1899. GP purchased the Crossett Lumber Company in 1962. The facility has separate pulping and bleaching lines to process hardwood and softwood. GP produces a variety of paper products, which include tissue paper and paper towels, on eight paper machines and two paper extruding machines. GP's Chemical Plant produces or produced paper chemicals, thermosetting resins, formaldehyde, and fractionates tall oil. The plants in the GP Complex share one process WWT system, through both manmade and earthen channels, eventually discharging to the Ouachita River, more than ten miles downstream of the GP Complex. Figure 1 shows the property boundaries of the GP Complex and WWT system. The primary residential areas are on the northern and eastern boundaries of the WWT system, as well as south of the GP Complex.

Figure 1. GP Property Boundary Map



Hydrogen Sulfide

Hydrogen sulfide (H₂S) is a chemical that is a gas at ambient pressure and temperature. It is a flammable, colorless gas with a foul odor, often described as a “rotten egg” smell. H₂S is a volatile chemical, meaning it easily evaporates into the air at normal temperatures. It is a reactive chemical, often oxidized to produce sulfuric acid (H₂SO₄) under common environmental conditions. H₂S can also cause damage to electrical contacts and other items that contain metals such as iron, copper and silver.

People can usually smell H₂S at low concentrations in air, ranging from 0.5 to 300 parts per billion (ppb). H₂S air concentrations from natural sources can range between 0.11 and 0.33 ppb. In urban areas, the air concentrations are generally less than 1 ppb. The chemical is immediately dangerous to life or health at a concentration of 100 parts per million (ppm), according to the National Institute for Occupational Safety and Health (NIOSH)². ATSDR has established acute (timeframes less than 14 days) and intermediate (14 to 365 days) MRL concentrations of 70 and

² NIOSH Pocket Guide to Chemical Hazards, <https://www.cdc.gov/niosh/npg/npgd0337.html>

20 ppb, respectively. EPA has established a chronic (lifetime) inhalation reference concentration (RfC) of 1.4 ppb³. People are primarily exposed to H₂S by breathing, and least likely exposed through ingestion. The effects of exposure depend on how much you breathe and for how long. A more detailed explanation about exposure and health risks can be found in Appendix A and on the Occupational Safety and Health Administration website (www.osha.gov/SLTC/hydrogensulfide/hazards.html).

It is well known that kraft pulp and paper mills emit foul smelling chemicals, specifically H₂S and other total reduced sulfur compounds (TRS). The chemical pulping technique and bleaching process uses harsh chemicals and high temperatures in order to process wood into a final product. The byproducts of this process include significant amounts of reduced sulfur compounds (sulfides). In addition, pulp and paper mills create a large amount of wastewater, even up to as much as 50 million gallons per day. According to Crawford, et al. (2009), while on-site stack emissions used to be considered the primary source of total reduced sulfur (TRS) emissions at paper facilities, it has been determined that WWT plants have increased contributions⁴.

In wastewater systems, H₂S can be generated through either chemical or biological pathways. The chemical production is dependent on factors such as pH, temperature, dissolved oxygen, and sulfide concentrations. Biological generation is the result of sulfur-reducing bacterial colonies in anaerobic environments having ample time and nutrients to produce H₂S as a byproduct. In general, the release of H₂S from the water into the air is facilitated by high levels of sulfides, high temperatures, low dissolved oxygen, turbulence, the presence of reducing agents, and low (acidic) pH levels.

Controlling H₂S levels in the air and water around a WWT system can be a complex, involving multiple challenges. Three common techniques for decreasing the generation of H₂S include chemical oxidation, precipitation, and pH elevation. Chemical oxidation could include the addition of chemicals such as hydrogen peroxide (H₂O₂) to react with the sulfides and increase the oxygen content of the water. However, this reaction is reversible, given the right conditions (such as agitation and increased temperatures). The addition of metallic salts (such as iron containing compounds) can cause a precipitation reaction, where the sulfides bind with the metal and turn into solids, thus reducing the amount of sulfides in the water. However, this reaction is not as effective at lower temperatures and could result in decreasing the pH of the water. Finally, keeping the pH of the water neutral or basic will decrease the potential for H₂S in the water to

³ US EPA Integrated Risk Information System (IRIS) Chemical Assessment Summary https://cfpub.epa.gov/ncea/iris/iris_documents/documents/subst/0061_summary.pdf

⁴ Crawford, R. J., Crapo, A. M., & Jain, A. K. (2009). Reduced sulfur compound emissions from kraft pulp and paper mill wastewater treatment plants. *Water Practice*, 3(1), 1-14.

become a gas. Often, sodium hydroxide (NaOH) is added to keep the pH greater than one. However, if the water undergoes turbulence or agitation, the H₂S can still enter the gas phase.

EPA's Passive H₂S Air Monitoring

In response to elevated readings in 2016 at GP's continuous H₂S air monitor, EPA Region 6 conducted six months of passive air monitoring on the facility grounds and in the nearby community from January to June 2017 to evaluate the sources and offsite impacts of H₂S from the facility's WWT system. EPA staff harvested samples on a biweekly basis and regularly shared the onsite data with GP and ADEQ. ADEQ accompanied EPA on some harvesting trips and GP conducted concurrent, collocated monitoring at the on-site locations. Meteorological data was obtained from a station installed on GP's facility for use with the continuous monitoring data. To ensure reliability and credibility of the measurements, the monitoring was conducted in accordance with the Quality Assurance Project Plan (QAPP), entitled "Georgia- Pacific CAA Investigations Monitoring Activities in EPA Region 6", dated December 14, 2016 (Appendix B).

Sample Site Selection

Site Assessment – September 2016

In order to determine the most appropriate siting of the passive monitors, an initial site assessment was conducted on September 27 and 28, 2016. EPA Region 6 staff and contractors visited the GP complex in Crossett to better understand the meteorological and topographical conditions, and to take measurements of the air and water along the WWT system. Using handheld Arizona Instruments Jerome J605 Hydrogen Sulfide Analyzers, portions of the WWT system and the paper mill were traversed on foot and analyzed for H₂S. The Jerome analyzers use gold film technology and can quantify H₂S as low as 3 ppb and as high as 10 ppm, with few interferences. The wastewater was also sampled for pH, dissolved oxygen, and temperature at multiple locations.

Jerome handheld monitors measured concentrations as high as 5.68 ppm along the WWT system, and concentrations as high as 8 ppm were observed on-site at the mill. Elevated concentrations were observed at the primary clarifier, the east ash basin, the exit of the surge basin, and Zones 1 and 2 of the Aeration Stabilization Basin (ASB). No H₂S was detected at the Outfall, Zone 4 of the ASB, or at GP's continuous air monitor. Stronger odors were observed at locations where the WWT stream is greatly agitated. Water sampling revealed multiple locations with pH less than 3 (acidic) and dissolved oxygen less than 1%.

Site Assessment – October 2016

A second site assessment was conducted October 26 and 27, 2016, utilizing EPA Region 5's Geospatial Monitoring of Air Pollution (GMAP) vehicle to monitor and evaluate ambient air in Crossett around the GP complex and WWT system. The GMAP uses a Picarro G2204 cavity ringdown spectroscopy (CRDS) analyzer and a DUVAS Model DV3000 UV multi-gas analyzer. The data are integrated with global positioning system location information and meteorological parameters when available to quantify air pollutant concentrations. The GMAP is able to collect multiple compounds, but EPA Region 6 focused primarily on H₂S ambient air concentration data. The monitored concentrations and final report (Appendix C) were used in determining the final site selection. Additional information about the GMAP can be found in the Standard Operating Procedures (SOP) and May13, 2016 QAPP (GMAP SOP R5-ARD-0002-r1; QAPP V3 2016-05-13).

Final Site Selection for Passive Sampling

A total of 20 sites were selected for EPA's passive monitoring, 9 locations on the fenceline or in the community (off-site) and 11 locations on GP's property (on-site). Monitoring locations were selected based on multiple considerations: proximity of residences to potential sources of H₂S, area wind patterns, availability of access, input from GP and the community, and the results of the two previously mentioned site assessments. Site IDs and descriptions can be found in Table 1 below. Figures 2 and 3 show the general locations of the off-site and on-site sampling locations, respectively.

Table 1. Passive Monitoring Sites

Site ID	Description of Location	On-site or Off-site
COM1	Adjacent to the east side of the GP continuous H ₂ S air monitor, north of the WWT system on the fenceline	Off-site
COM2	In a community north of the WWT system, near S. Wall Road and 2 nd Avenue	Off-site
COM3	In a community east of the WWT system, on Dunmore Loop	Off-site
COM4	In a community east of the WWT system, near N. Missouri Street and 6 th Avenue, Clemmie Wimberly Athletic Park baseball field	Off-site
COM5	East of the GP entrance gate to WWT system, near Westview Cemetery	Off-site
COM6	In a community east of the WWT system, near Bethea Road	Off-site
COM7	On west fenceline of GP Complex, near Hancock Road and McDougal Road	Off-site
COM8	In a community north of WWT system, near Hwy 82 west of Thurman Road	Off-site
THUR	North of the GP entrance gate to WWT system on Thurman Road	Off-site
MILL	On west boundary of GP Complex, 30 feet west of where wastewater sewers are piped underground, near Hancock Rd.	On-site
PCLR	Primary Clarifier, north part of WWT system	On-site
CONV	Convergence of all wastewater streams, south/downstream of the Primary Clarifier	On-site
EABI	East Ash Basin Inlet	On-site
WABI	West Ash Basin Inlet	On-site
EABO	East Ash Basin Outlet	On-site
WABO	West Ash Basin Outlet	On-site
SBO	Surge Basin Outlet, south side of basin approximately 20 feet above water level	On-site
ASB1	Aeration Stabilization Basin, between zones 1 and 2	On-site
ASB2	Aeration Stabilization Basin, south of zone 2	On-site
OUT	Outfall at southwest corner of WWT system	On-site

Figure 2. Map of Off-Site Sampling Locations, Crossett, AR

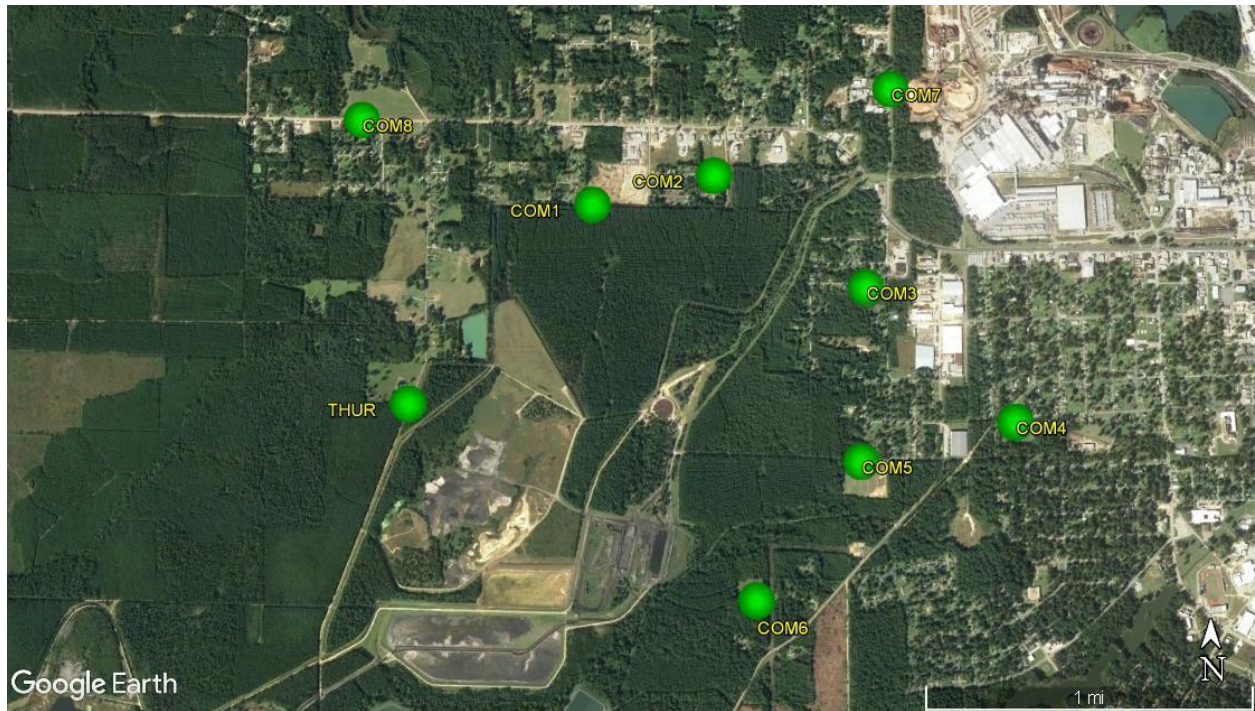
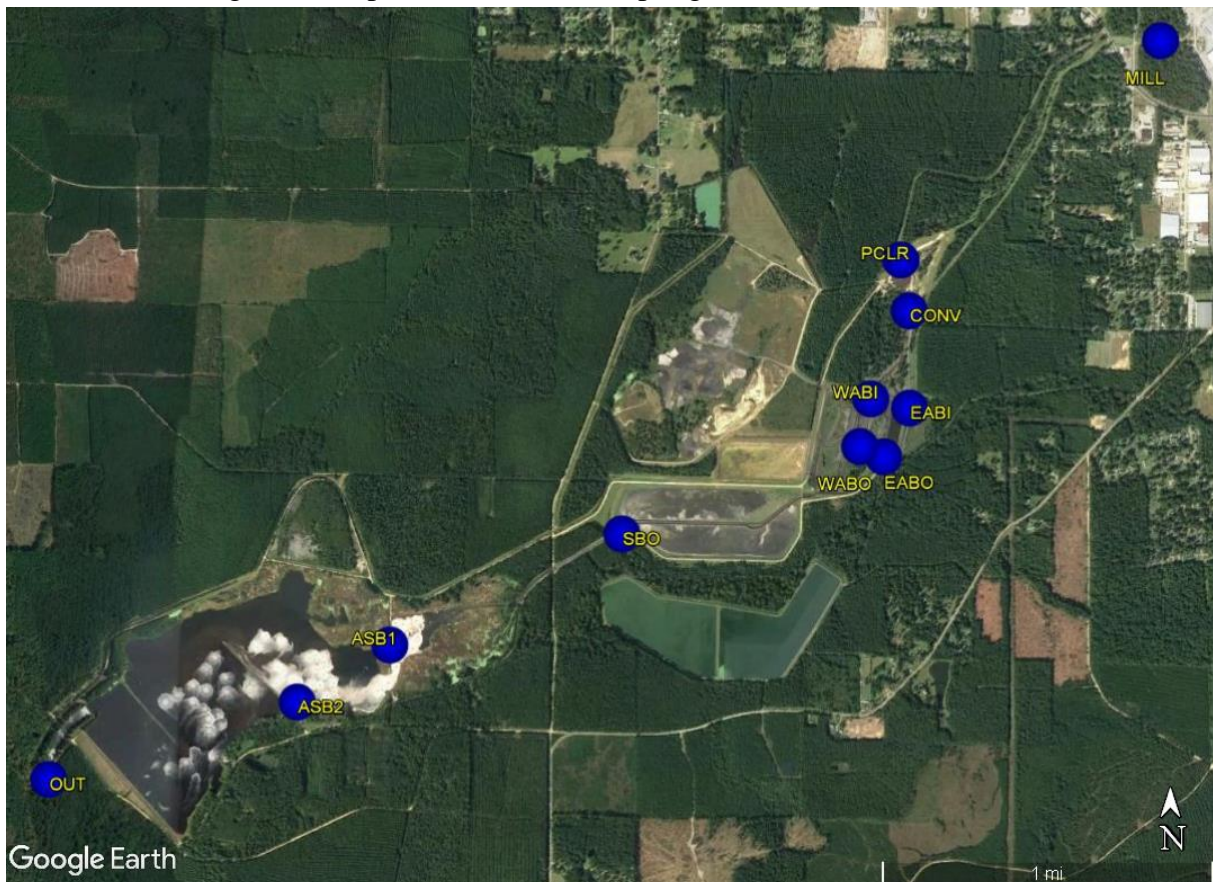


Figure 3. Map of the On-Site Sampling Locations, Crossett, AR



Methodology

Passive monitoring was performed using Radiello diffusive air samplers (Sigma-Aldrich). H₂S air samplers were deployed at each site biweekly from January 13 to June 30, 2017. Passive monitoring does not require the use of a pump, and instead collects molecules onto an adsorbent cartridge as the air flows by. Each adsorbent cartridge is placed inside a diffusive body for protection from large particles and is mounted on a triangular support plate. The cartridge is further protected by being placed in a shelter, which shields the cartridge from weather elements and direct sunlight. The adsorbent cartridge is coated with zinc acetate, which reacts with the H₂S in the air to form a stable compound, zinc sulfide. The sample is extracted and analyzed by spectrophotometry. Samples were sent to ALS Environmental laboratories in Cincinnati, OH for analysis.

Using the average ambient temperature and total minutes of exposure, each two-week average concentration of H₂S is calculated. A detection limit is defined as the lowest concentration of a component that can be reliably detected with a given analytical method. For this project, the detection limit is 0.57 ppb. For quality assurance, a field blank was kept at the COM1 site and a duplicate (collocated) sample rotated locations (Appendix B, page A-6). The temperature data was retrieved from the previously mentioned meteorological station. Details about the laboratory analysis and calculations can be found in the QAPP (Appendix B, page D-1).

Results

EPA had 12 episodes of sample collection from each location from January 13, 2017 to June 30, 2017. Table 2 shows the date range and average temperature for each episode. Of the 240 primary samples, two samples were invalidated due to equipment malfunction. Collocated samples were evaluated to validate the data collected. Comparing the relative percent difference (RPD) of all the collocated samples to the primary samples collected, the average RPD is 12%. Values are considered statistically the same if the RPD is less than 20%, so this value is within the acceptable quality range.

Table 2. Passive H₂S Air Monitoring Episode Dates and Average Temperature

Episode #	Start Date	End Date	Average Temperature (°C)
1	1/13/2017	1/27/2017	13.4
2	1/27/2017	2/10/2017	10.5
3	2/10/2017	2/24/2017	15.1
4	2/24/2017	3/10/2017	14.7
5	3/10/2017	3/24/2017	14.4
6	3/24/2017	4/7/2017	19.0
7	4/7/2017	4/21/2017	20.5
8	4/21/2017	5/5/2017	18.6
9	5/5/2017	5/19/2017	21.5
10	5/19/2017	6/2/2017	22.0
11	6/2/2017	6/16/2017	24.3
12	6/16/2017	6/30/2017	25.6

The results for the on-site and off-site locations for each 2-week episode are shown in Tables 3 and 4, respectively. Because the samples were collected for two week periods, the results represent average concentrations for that time period and do not reveal if higher concentrations may have occurred over shorter timeframes. “ND” indicates that the concentration was below the detection limit of 0.57 ppb for that sampling event. “NA” indicates that the sample was invalidated and no data is available for that sampling event.

Table 3. Two-Week Average Concentrations of H₂S (ppb) for On-Site Facility Locations

Episode	MILL	PCLR	CONV	EABI	WABI	WABO	EABO	SBO	ASB1	ASB2	OUT
1	6.2	32	16	52	25	62	70	100	51	21	1.3
2	22	56	41	98	110	120	61	89	76	34	3.0
3	37	65	34	35	38	77	15	72	84	44	4.8
4	9.1	30	30	21	81	63	29	82	96	89	6.6
5	11	20	16	62	96	72	66	100	70	59	3.3
6	5.5	44	16	69	93	61	69	110	96	9.5	1.2
7	6.0	30	13	99	110	88	76	84	100	19	1.2
8	1.4	47	6.5	95	NA	99	38	90	78	14	ND
9	0.92	6.4	4.2	6.9	93	40	1.5	83	36	7.9	ND
10	2.6	11	7.1	36	81	71	20	77	76	5.4	ND
11	3.1	13	5.2	48	32	59	74	81	64	26	1.3
12	6.7	7.6	5.8	92	32	82	91	92	78	30	2.4

Table 4. Two-Week Average Concentrations of H₂S (ppb) for Off-Site Community Locations

Episode	COM1	COM2	COM3	COM4	COM5	COM6	COM7	COM8	THUR
1	1.3	0.59	ND	ND	0.69	2.1	ND	0.84	5.3
2	7.6	6.9	5.6	2.6	6.7	3.9	4.9	14	39
3	3.2	1.3	2.0	0.95	2.2	2.1	1.4	4.8	4.7
4	3.3	2.2	1.8	ND	1.4	1.3	1.7	3.0	9.6
5	3.5	1.5	0.77	ND	ND	ND	1.1	3.5	10
6	2.0	0.96	0.72	ND	1.1	2.3	3.4	2.1	7.0
7	1.6	1.5	0.76	ND	1.1	1.1	1.2	7.2	12
8	0.99	NA	0.74	0.82	2.4	2.8	ND	1.7	5.0
9	0.96	ND	ND	ND	ND	ND	ND	1.4	3.7
10	0.94	ND	ND	ND	0.92	1.2	ND	0.81	1.4
11	0.92	0.61	ND	ND	ND	ND	ND	3.8	5.1
12	ND	ND	ND	ND	ND	ND	ND	0.75	1.9

Table 5 ranks the average H₂S concentrations for the entire six-month project from highest to lowest. To calculate the average H₂S concentration at each location for the sampling period, EPA utilized the following protocols to define numeric values for those samples that did not have measurable H₂S concentrations (“ND” or non-detect samples):

- For locations with five or less non-detect sample concentrations, the ND datum was assigned a value of 0.285 ppb, which is one-half of the detection limit of 0.57 ppb.
- For locations with six or more non-detect sample concentrations, the ND datum was assigned a value of 0.0 ppb.

Table 5. Twenty-Four-Week Average H₂S Concentrations (ppb) for Each Location

Site	Average H ₂ S concentration (ppb)
SBO	88
ASB1	75
WABO	75
WABI	72
EABI	59
EABO	51
PCLR	30
ASB2	30
CONV	16
MILL	9.3
THUR	8.7
COM8	3.7
COM1	2.2
OUT	2.2
COM6	1.6
COM2	1.5
COM5	1.5
COM3	1.2
COM7	1.1
COM4	0.4

When further analyzing the data, it becomes apparent that the first 8 episodes are distinctly different than episodes 9 through 12. GP experienced an outage from approximately April 29 to May 13, 2016, reducing the volume and characteristics of the waste sent to the WWT system. Normal operations may have been altered toward the end of the monitoring project. As seen in Table 6, almost every site experiences a decrease in average concentration from Episodes 1-8 to Episodes 9-12. Only sites SBO and EABO experienced decreases that were not statistically significant.

Table 6. Comparison of Average H₂S Concentrations (ppb)
for Each Location for Episodes 1-8 and 9-12.

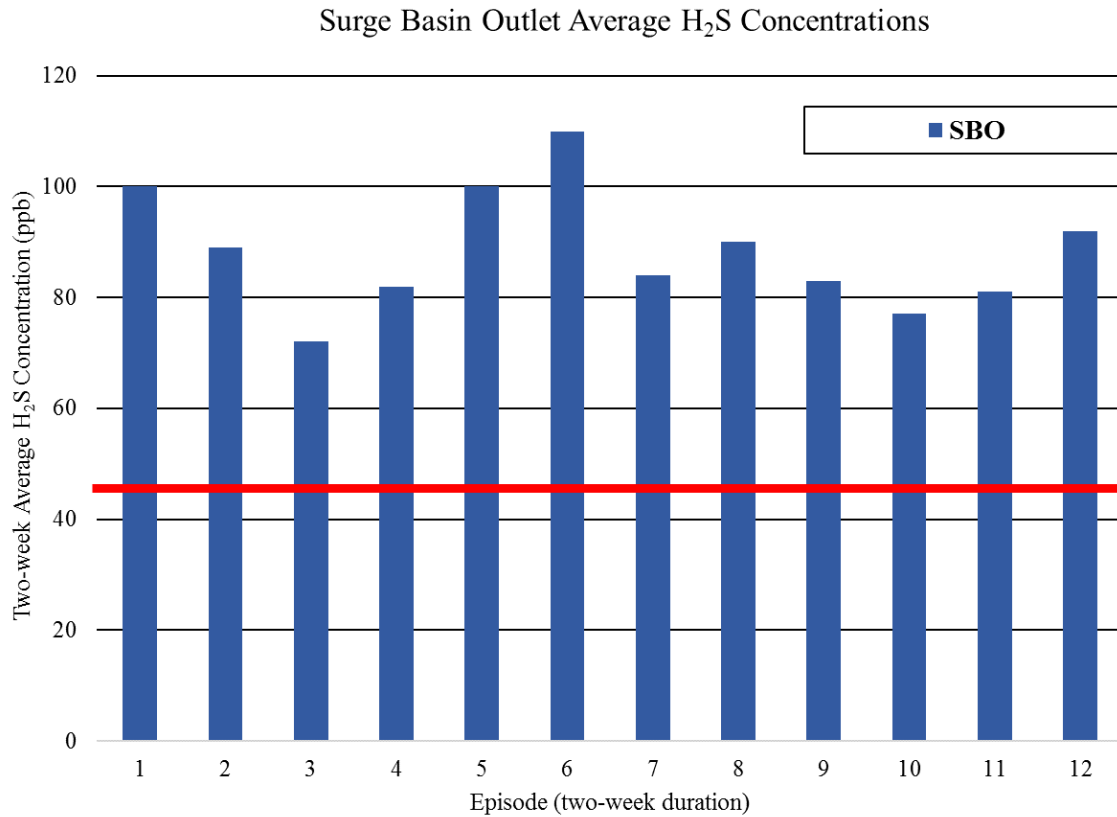
Site	Average H₂S Concentrations (ppb) Episodes 1-8	Average H₂S Concentrations (ppb) Episodes 9-12	Relative % Difference
SBO	91	83	8.8
ASB1	81	64	25
WABO	80	63	24
WABI	79	60	28
EABI	66	46	37
EABO	53	47	13
PCLR	41	9.5	124
ASB2	36	17	70
CONV	22	5.6	118
MILL	12	3.3	115
THUR	12	3.0	117
COM8	4.6	1.7	93
COM1	2.9	0.78	116
OUT	2.7	1.1	87
COM2	2.1	0.37	141
COM6	2.0	0.59	108
COM5	2.0	0.44	127
COM7	1.7	0.00	200
COM3	1.6	0.29	139
COM4	0.55	0.00	200

Surge Basin Outlet (SBO)

The Surge Basin is a large, open channel used to control the rate at which water enters the Aeration Stabilization Basin (ASB). At the SBO, there are mechanical gates and a pH monitor, and chemicals can be added to adjust biological activity and pH. At the outlet, the water experiences increased agitation. The data shows that the SBO location not only had the highest overall average, each episode had a concentration that exceeded 70 ppb. The overall average H₂S concentration for all on-site locations over 6 months is 46 ppb. This average is noted by a thick red line in Figure 4. Multiple factors can contribute to elevated concentrations, including increased biological activity and agitation. Episode 3 had the lowest concentration, 72 ppb. Five

on-site locations, and all nine off-site locations, experienced a statistically significant decrease from episode 2 to episode 3.

Figure 4. Two-Week Average Concentrations of H₂S (ppb) for SBO



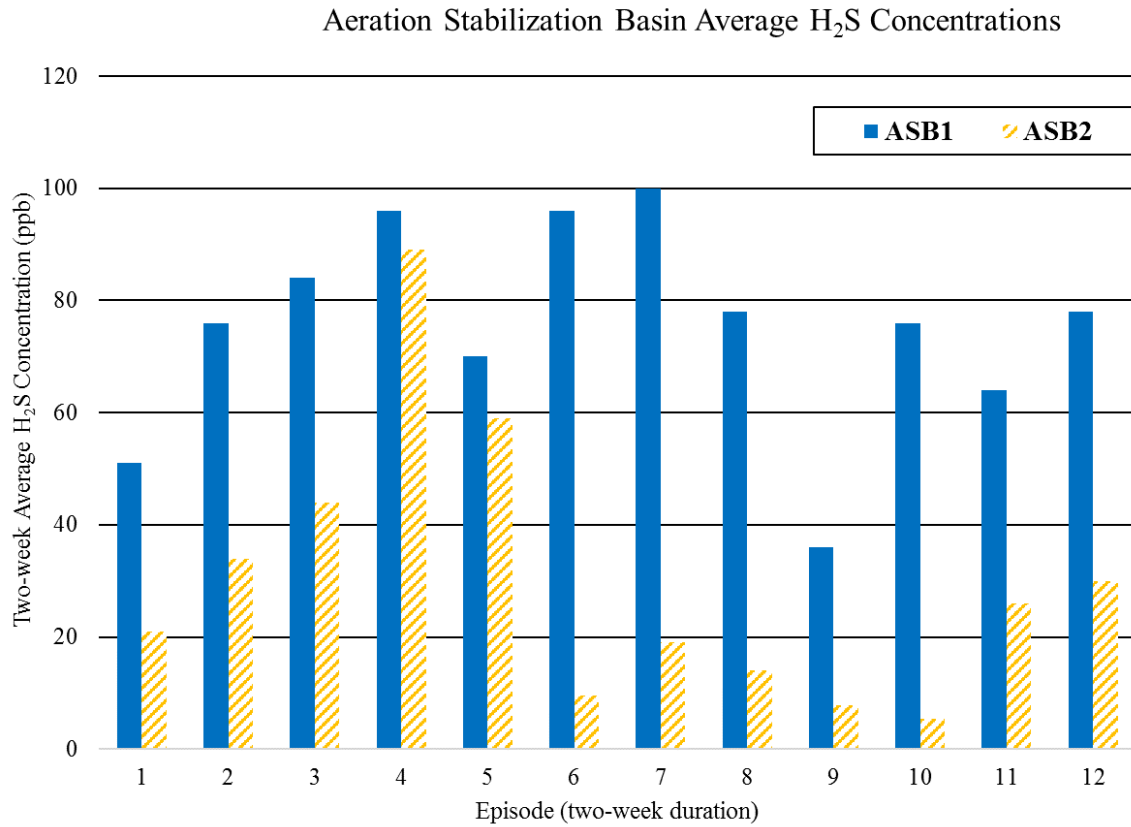
Aeration Stabilization Basin (ASB)

The final stage of GP's WWT system is a large Aeration Stabilization Basin (ASB) (approximately ½ square mile in area) with four zones. Zone 1 has the most mixing and aeration, which decreases until Zone 4 where the water is calm and the settling of solids can occur. In the ASB, the wastewater undergoes biological degradation in aerobic conditions. The settled solids are periodically dredged, dewatered, and trucked to a landfill.

The ASB1 sampling location was stationed on a peninsula between Zones 1 and 2. This location had the second highest overall H₂S concentration measured in this project. The ASB2 sampling location was stationed south of Zone 2. As expected, the concentrations were consistently lower than ASB1, as the typical wind direction flows to the north. The two-week concentrations for ASB1 and ASB2 are visualized in Figure 5. Due to ample aeration, it is unlikely that the H₂S

produced in the ASB is due to biological pathways. Rather, increased agitation may reduce the effectiveness of chemical oxidizers used upstream.

Figure 5. Two-Week Average Concentrations of H₂S (ppb) for ASB1 and ASB2



East and West Ash Basins

The primary function of ash basins is to slow the flow of wastewater so the solid portions may settle, separate, and be removed. The water flows into either the East or West Ash Basin, alternating on a five- to six-week cycle. The unused Ash Basin is blocked, drained, and the remaining ash and sludge is mechanically dredged, dewatered, and transported to a landfill.

The two-week concentrations are visualized in Figures 6 and 7 below for the East Ash Basin and West Ash Basin, respectively. No valid sample was available for episode 8 at the WABI. As previously mentioned, GP experienced an outage from April 29 to May 13, approximately. The outage could be related to the significant decrease observed at EABI, EABO, and WABO for episode 9. However, the East Ash Basin was closed and the West Ash Basin was open during this time.

As seen in Figures 6 and 7, there is no obvious pattern in the ash basin H₂S concentrations. There is variability when comparing inlet versus outlet and the east versus the west. It was expected that the inlets would consistently be greater than the outlets, due to typical wind patterns, however this was not observed. By evaluating the percent relative differences between the inlets and outlets, EABI had higher concentrations than EABO for 6 out of 12 episodes and WABI had higher concentrations than WABO for 5 out of 11 episodes.

When an ash basin is closed, the potential for biological production of H₂S is increased. Due to the alternating ash basin closure cycle, it was expected that greater concentrations would be observed at the unused ash basin. If the inlet and outlet concentrations are averaged together, the total East Ash Basin concentrations exceed the total West Ash Basin only for episodes 1, 11, and 12. The West Ash Basin had higher concentrations than the East Ash Basin for episodes 2, 3, 4, 5, 9, and 10. Episodes 6 and 7 were statically equal. It is not immediately clear whether the greatest influence of H₂S emissions is from biological (anaerobic) conditions or the chemical (pH, temperature, and/or sulfur concentration) conditions.

Figure 6. Two-Week Average Concentrations of H₂S (ppb) for EABI and EABO

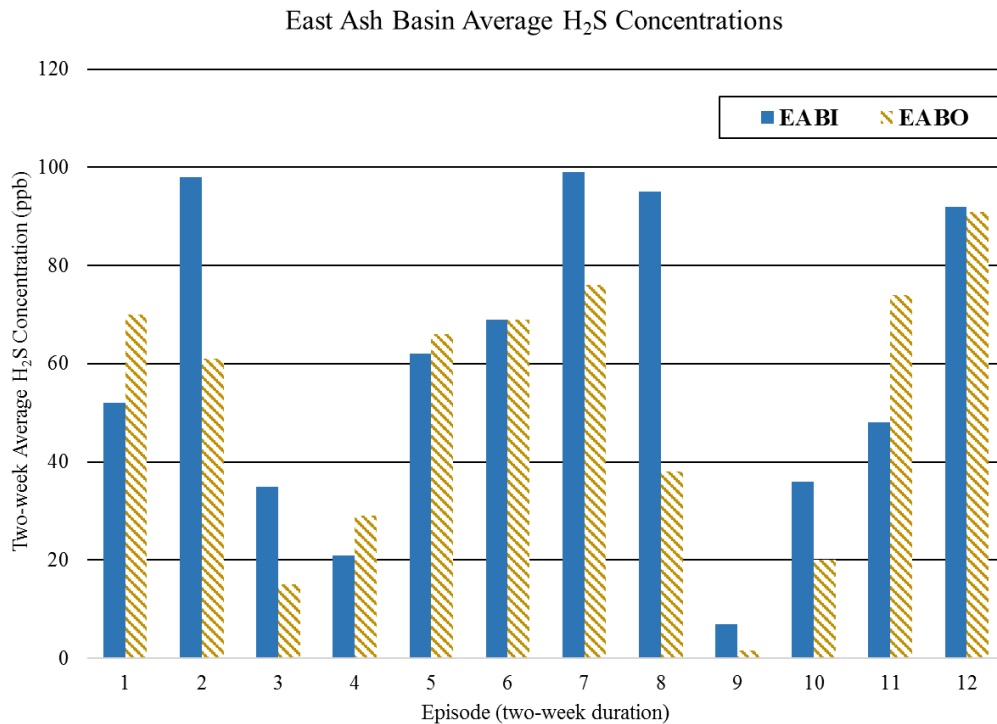
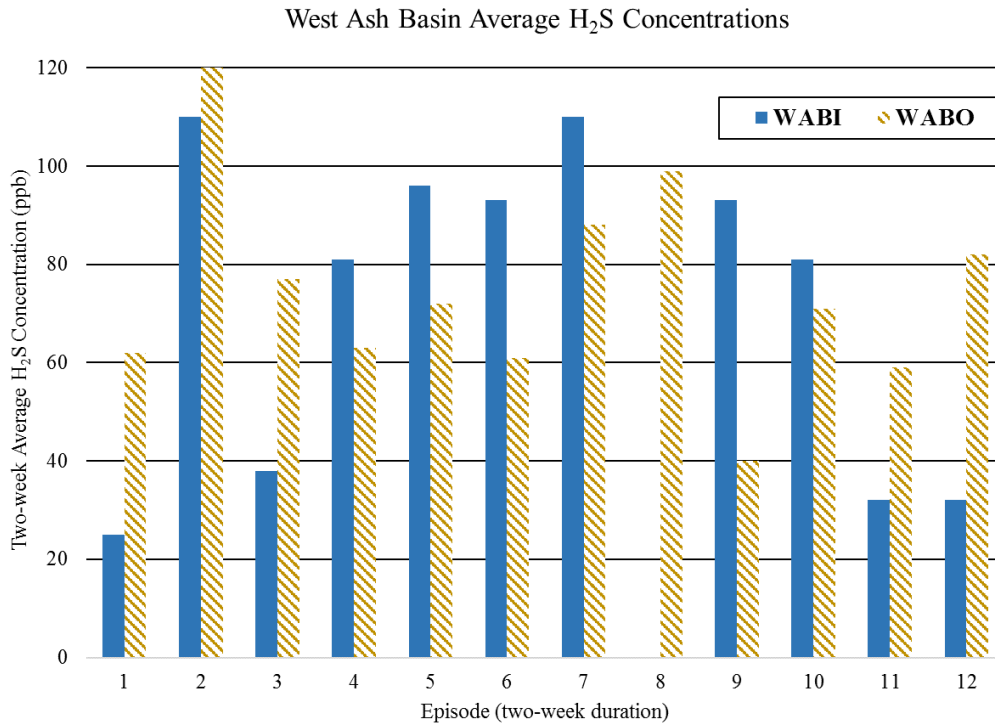


Figure 7. Two-Week Average Concentrations of H₂S (ppb) for WABI and WABO



Community Monitors

Nine of the twenty sampling sites were located on the fenceline and in the community. THUR and COM1 were on the northern fenceline of the WWT system, and COM5 was on the east fenceline. The residential monitors were placed in neighborhoods to the north and east of the WWT system. The typical wind direction in Crossett flows from south to north; therefore, no off-site monitors were placed to the south or west of the WWT system. Bar graphs for each off-site community monitor can be found in Appendix D.

As seen in Tables 5 and 7, the concentrations for the eastern community monitors decreased from west to east. COM4 was the furthest east, and experienced only 3 episodes above the detection limit. THUR had the highest concentrations of all the off-site monitors, and exceeded the ATSDR intermediate MRL once (episode 2). COM8, located 1-mile north of the fenceline, experienced the second highest H₂S concentrations.

Table 7. 24-Week Average, Single Episode Minimum, and Single Episode Maximum H₂S Concentrations (ppb) at Off-Site Community Locations

Site ID	24-week Average	Single Episode Minimum	Single Episode Maximum
THUR	8.7	1.4	39
COM8	3.7	0.8	14
COM1	2.2	ND	7.6
COM6	1.6	ND	3.9
COM2	1.5	ND	6.9
COM5	1.5	ND	6.7
COM3	1.2	ND	5.6
COM7	1.1	ND	4.9
COM4	0.4	ND	2.6

Air Dispersion Modeling

Model Comparisons and Source Apportionment

At the request of EPA Region 6 staff, the Office of Air Quality Planning and Standards (OAQPS) provided air dispersion modeling support in order to estimate emission rates and identify the most likely WWT emission points. For all dispersion modeling, OAQPS used the AERMOD⁵ dispersion modeling system. AERMOD is EPA’s preferred model for near-field dispersion modeling. Detailed information about modeling inputs can be found in Appendix A.

As previously mentioned, data collected during the first 8 episodes are distinctly different than episodes 9 through 12. Therefore, only data from January 13 to May 5, 2017 was used in the modeling in attempt to reflect typical GP operations. In general, the model tended to under-predict ambient levels. Table 8 (adapted from Table 3 of Appendix A) presents the average concentrations measured and predicted by the AERMOD model for the first 8 episodes, as well as the monitor to model ratios. Ratios greater than 1 indicate that the monitored values observed exceed the modeled values, ratios less than one indicate that the monitored values observed were less than the modeled values. In general, the model is in good agreement with the observed concentrations. However, concentrations at the CONV, MILL, and OUT sites were found to be 5 to 8 times above modeled estimates for episode 2. This pattern may indicate an increased loading of TRS compounds entering the WWT system or generation of increased H₂S from biological

⁵ Air Quality Dispersion Modeling – Preferred and Recommended Models <https://www.epa.gov/scram/air-quality-dispersion-modeling-preferred-and-recommended-models>

activity. In addition, on-site parameters such as process water temperature, ambient air levels, water flow, and basin retention times are not well documented.

Table 8. H₂S Monitor to Model Ratios for On-site Facility Monitors

Site ID	Average Passive Monitoring Value (µg/m ³)	Average Modeled Value (µg/m ³)	Monitor to Model Ratios
ASB1	114	87	1.3
ASB2	51	28	1.8
CONV	30	10	3.0
EABI	93	88	1.1
EABO	74	87	0.9
MILL	17	14	1.2
OUT	3.8	1.0	3.8
PCLR	57	69	0.8
SBO	127	84	1.5
WABI	97	116	0.8
WABO	112	103	1.1

Nine on-site locations were considered in estimating H₂S emissions sources: ASB1, MILL, PCLR, EABO, EABI, WABO, WABI, SBO, and the GP Complex itself. Table 9 summarizes the modeled emissions associated with each WWT source and the GP Complex (adapted from Table 4 of Appendix A). A review of the Toxic Release Inventory (TRI) for 2016 provided by GP, shows close agreement with the model’s estimated total WWT emissions of 126 TPY H₂S, with respective TRI release amount of 159 TPY⁶. While the SBO showed the greatest concentrations of H₂S, due to the small area size of the outlet, it is not modeled to be the greatest source of total H₂S emissions.

⁶ 2016 TRI Form R from GP for hydrogen sulfide;
https://oaspub.epa.gov/enviro/tri_formr_partone_v2.get_thisone?rpt_year=2016&dcn_num=1316215662584&ban_flag=Y

Table 9. Estimated H₂S Emission Rates

Location or Site ID	Emission Rate (TPY)
GP Complex	13.9
ASB1	60.6
MILL	23.4
PCLR	11.1
EABO	2.0
SBO	1.0
WABO	7.8
EABI	4.2
WABI	1.6

Community Health Considerations

A detailed explanation of health benchmarks associated with chronic and acute inhalation exposure to H₂S can be found in Appendix A. To evaluate the potential for community health impacts, the AERMOD model was run, using the emissions from Table 9, for the time period between January 2014 – July 2017. For the purposes of this analysis, the three-and-a-half-year time period was assumed to be representative of someone’s long-term (70-year lifetime) average exposure. It is important to note that this approach assumes that the emissions estimated above occur continuously for this entire time period.

When comparing the average ambient levels for the three-and-a-half-year period to the EPA RfC for H₂S (1.4 ppb), the AERMOD model predicts ambient levels on-site and adjacent to the GP facility up to 50 times the RfC. However, in these industrial locations, we would not expect human exposures to be continuous over an extended period of time (i.e., not a residential location). When we look farther away from the GP facility in the nearby residential community, the AERMOD model is predicting ambient levels up to 2-3 times the chronic EPA RfC.

When examining the potential for 1-hour impacts, the model predicts ambient levels above the 1999 California Reference Exposure Level of 30 ppb at most off-site locations, and slightly above the National Advisory Committee Acute Exposure Guideline Level (AEGL)⁷ Level 1 value (510 ppb) at the on-site locations. No predicted value exceeded or approached concentrations at which the general population could experience irreversible or other serious, long-lasting adverse health effects, as defined by the AEGL-2 (27,120 ppb).

⁷ Hydrogen sulfide results – AEGL Program <https://www.epa.gov/ae-gl/hydrogen-sulfide-results-ae-gl-program>

The model and the passive monitors show ambient levels above the odor threshold value at many locations. Thus, the continued public awareness of H₂S odors in the ambient air is reasonable. It's important to consider that even though the modeling performed here is estimating ambient levels above the stated health benchmark values, that other exposure factors, such as time spent in indoor locations or away from the home, have not been considered in this analysis.

Conclusions

Based on this six-month air monitoring project, the main sources of H₂S along the WWT system were observed to be the ash basins, aeration stabilization basin, and the surge basin. Because the wind direction is from the south, the highest concentrations of H₂S were observed north of those WWT system features. It is not clear if the observed decrease from episodes 1-8 to episodes 9-12 is a result of altered facility operations or seasonal conditions. The modeling performed assumes that the emissions from January 13 to May 5, 2017 reflect typical GP operations, and are just estimations.

While this air sampling was not designed to evaluate risk to individuals from H₂S at specific locations, it does provide measurements that can be used in comparison with health benchmark values. The ATSDR intermediate MRL of 20 ppb was exceeded once at an off-site monitoring station: THUR (episode 2). All off-site locations were below 20 ppb when averaged over the entire 6-month monitoring period. Air modeling predicts ambient concentrations up to 2-3 times the chronic (lifetime) EPA RfC of 1.4 ppb.

For more information about H₂S health effects, a copy of the Agency for Toxic Substances and Disease Registry (ATSDR) *Fact Sheet on Hydrogen Sulfide* is attached as Appendix E.

EPA Region 6 is using the data collected from this monitoring project in discussions with GP in the hope that projects and practices developed will lead to further reductions of airborne H₂S along the WWT system and in the adjacent neighborhoods.

APPENDICES